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(54) **Organosiloxane/metal oxide coatings.**

(57) An organoalkoxysilane/alumina sol-gel composition and method for its production are disclosed whereby an aluminum alkoxide is hydrolyzed in water to form a sol, to which is added a hydrolyzable organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is at least 1 and less than 4. The composition is dried and cured to form an organosiloxane/alumina monolith or coating on a substrate. An organoalkoxysilane/metal oxide sol-gel composition and method for its production are disclosed whereby an organoalkoxysilane is partially hydrolyzed in organic solution and reacted with alkoxide of the general formula $M(OR'')_4$ wherein M is aluminum, titanium, zirconiu, etc. or mixtures thereof and R'' is a lower alkyl radical. The composition is hydrolyzed, dried and condensed to form an organosiloxane/metal oxide abrasion-resistant coating on a substrate. An ultraviolet radiation resistant coating is disclosed comprising cerium oxide in an inorganic oxide matrix formed by the hydrolysis and condensation of an alkoxysilane and/or other metal alkoxide. A method is disclosed for making an organoalkoxysilane/metal oxide sol-gel composition in an essentially aqueous medium by partially hydrolyzing an organoalkoxysilane with a limited amount of water which is essentially completely consumed in the hydrolysis reaction, adding a metal alkoxide of titanium or zirconium to the essentially anhydrous partially hydrolyzed organoalkoxysilane, completely reacting the metal alkoxide with

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the partially hydrolyzed organoalkoxysilane to form an oxide network and then completely hydrolyzing the composition in water. A method of removing residual organic material from inorganic polymers prepared from alkoxides by a sol-gel process is disclosed, wherein the dried gel is treated with aqueous fluid to effect solid-state hydrolysis of residual alkoxy groups. Organic-inorganic hybrid polymers and a method of making them by reaction of organic monomers with organofunctional alkoxysilanes are disclosed. A composition and method are disclosed for forming an oxide film containing silicon and tin on a substrate surface involving a composition comprising a partially hydrolyzed alkoxysilane and an organotin compound, and thermal reaction thereof.

ORGANOSILOXANE/METAL OXIDE COATINGS

Field of the Invention

The present invention relates generally to the art of abrasion-resistant coatings, and more particularly to the art of abrasion-resistant inorganic coatings on abrasion-prone organic substrates.

Background

A number of patents to Yoldas and other dislose sol-gel compositions containing various components. U.S. Patent Nos. 3,941,719 and 3,944,658 to Yoldas relate to alumina sol-gels. U.S. Patents No. 4,208,475 and 4,244,986 to Paruso and Yoldas describe a liquid polymer formed from organometallic sodium and aluminum compounds.

U. S. Patent No. 4,271,210 to Yoldas discloses a method of forming an optically clear, porous metal oxide layer having a low refractive index on a glass substrate by dipping the substrate into a clear colloidal solution of metal alkoxide.

U.S. Patent No. 4,278,632 to Yoldas discloses a method of forming a clear vitreous gel of silica-titania binary by preparing a clear organic solvent solution of partially hydrolyzed alkoxide of either silicon or titanium and then adding the other element in the form of alkoxide or a clear organic solvent solution of partially hydrolyzed alkoxide. The components are reacted, additional water is added to complete hydrolysis and the resulting product is then dried and heated to remove residual organic material.

U. S. Patent No. 4,286,024 to Yoldas discloses a high temperature resistant transparent monolithic member or coating consisting of aluminum and silicon in a ratio of about 2:1 and in reacted oxide form, formed by reacting precursor alkoxides of aluminum and silicon in the presence of water to form a clear solution, gelling the reacted precursors, and drying the gel in the form of a monolithic member or coating on a substrate. The dried material is then heated to evolve all residual hydrogen, carbon and water and to eliminate porosity.

U.S. Patent No. 4,346,131 to Yoldas discloses polymerized solutions for depositing optical oxide coatings prepared by reacting metal alkoxide with a mixture of critical amounts of water and/or acid in an alcohol medium. The alkoxides may be titanium, tantalum and/or silicon.

According to these patents, hydrolytic polycondensation of metal alkoxides produces polymeric species containing alkoxy and hydroxyl pendent and terminal groups. Typical sol-gel compositions contain about 10 to 40 percent by weight organic and hydroxyl components. Heat treatment is carried out at sufficiently high temperature, generally around 500°C, to remove residual organic material.

Optical quality abrasion resistant coated plastic materials generally require a coating that protects the substrate from the damaging effects of ultraviolet (UV) radiation. Protection from ultraviolet radiation is especially important for polycarbonate, since hydrolytic degradation is apparently accelerated by UV exposure. Conventional UV stabilizers do not impart sufficient protective capacity to abrasion resistant coatings, as sufficient amounts of most typical organic UV absorbers cannot be added to abrasion resistant coatings without adversely affecting hardness and adhesion of the coating. Moreover, typical UV absorbers may gradually become deactivated after prolonged exposure, and also may gradually be leached from the composition.

Summary of the Invention

The present invention provides an abrasion-resistant coating composition comprising an organoalkoxysilane and a hydrolyzable compound of a metal such as titanium or zirconium. Such a composition is formed by producing active soluble and polymerizable titanium or zirconium species from titanium or zirconium alkoxides and dispersing or polymerizing the titanium or zirconium species into silicon-oxygen networks of organosiloxane polymers via reaction with silanol groups. The presence of titanium or zirconium in the polymer network modifies such properties as the hardness and refractive index of the polymer. When such a titanium or zirconium modified polymer coating is applied to a plastic substrate surface, the coating increases the chemical resistance, index of refraction and blocking of ultraviolet radiation, in addition to the abrasion resistance.

The present invention also involves the preparation of silane/alumina sol-gel compositions by adding an organoalkoxysilane into an aqueous alumina sol prepared from a hydrolyzable aluminum alkoxide. The organoalkoxysilane hydrolyzes and condenses with the hydrolyzed aluminum alkoxide to form a siloxane/alumina copolymer with an organic constituent. The organosiloxane/alumina compositions of the present invention may further comprise a pigment or blend of pigments in order to form a non-porous durable paint which can be applied by conventional methods and cured conveniently at temperatures as low as 80°C.

The present invention, in addition to providing abrasion resistance, involves also optimizing a variety of properties such as alkali resistance, adhesive strength, chemical resistance, water stability and index of refraction for optical coatings. The present invention encompasses a multi-component system combining an organoalkoxysilane composition with a combination of other components such as hydrolyzable alkoxides of aluminum, titanium, tantalum, hafnium and the like to form an inorganic oxide polymer network optimizing overall performance. The organoalkoxysilane/mixed metal alkoxides composition can be coated on glass, metals and ceramics, as well as on plastics, not only for abrasion resistance, but also for chemical resistance, e.g., to alkali or oxidation. The organoalkoxysilane/mixed metal alkoxides composition may also function as a carrier and binder for pigments to form opaque and/or colored coatings. An important feature of the present invention is that the proportion of metal alkoxides can be selected to produce a coating with a desired refractive index, e.g., to match a transparent substrate.

The present invention provides protection for underlying plastic substrates such as polycarbonate from damaging ultraviolet radiation by means of transparent coatings containing cerium oxide, a stable strongly ultraviolet absorbing species. The transparent cerium oxide containing UV protective coatings of the present invention are formed from aqueous sols containing colloidal cerium oxide in addition to alkoxides of silicon and/or other metals which hydrolyze and polymerize by condensation to form a film in which the cerium is incorporated in the oxide network of the coating.

The present invention further provides a method for incorporating metal such as titanium or zirconium into the polymer network structure of an organoalkoxysilane in an aqueous medium. The method of the present invention involves initial partial hydrolysis of the organoalkoxysilane, reaction of a metal alkoxide of titanium or zirconium with essentially anhydrous partially hydrolyzed organoalkoxysilane, and final complete hydrolysis of the sol-gel composition. The aqueous compositions of the present invention deposit harder, more abrasion-resistant, and higher optical quality coatings than organic solvent compositions.

The present invention provides for the removal of residual organic material from sol-gel compositions by means of chemical reaction at or near ambient temperature by treating a formed gel monolith or thin film with water, containing a catalyst if needed, to effect solid-state hydrolysis of residual organic groups. By avoiding removal of organic material from sol-gel compositions by means of thermal decomposition, the present invention prevents gel degradation and carbon deposits which adversely affect sol-gel compositions. Further, since high temperatures are avoided, application of sol-gel compositions is not limited to high temperature resistant substrates in accordance with the present invention. Furthermore, polymerization and densification continues in the solid state under the conditions of the present invention.

Organic-inorganic hybrid polymers in accordance with the present invention are prepared by polymerizing an organic monomer in the presence of an inorganic oxide sol comprising an organoalkoxysilane having an organic functional group capable of reacting with said organic monomer.

Transparent oxide films containing silicon and tin are applied to glass by spraying on a hot glass surface an alcohol sol containing partially hydrolyzed alkoxysilane and an organotin compound in accordance with the present invention.

Detailed Description of the Preferred Embodiment

A sol-gel system for producing an organosiloxane/alumina composition may be prepared in the following manner. First, an aluminum alkoxide is hydrolyzed using water as solvent. The temperature is preferably maintained at about 80°C during hydrolysis to prevent the formation of insoluble bayerite. Various hydrolyzable aluminum alkoxides may be used to form a sol in accordance with the present invention. Preferably, aluminum alkoxides are of the general formula $Al(OR)_3$, wherein R is preferably an alkyl radical of the general formula C_nH_{2n+1} wherein n is from 2 to 4. Aluminum isopropoxide is a particularly preferred aluminum alkoxide. Preferably, aluminum isopropoxide is added to water which has been heated to 80°C, followed by an acid hydrolyzing agent. Various acids may be used in accordance with the present invention; both inorganic acids, such as nitric and hydrochloric acids, and organic, such as acetic and dichloroacetic acids. The basic hydrolysis reaction is illustrated below.

$Al(OR)_3 + yH_2O \rightarrow Al(OR)_{3-y}(OH)y + yROH$

The condensation reaction may involve alkoxy and/or hydroxyl groups, and produce water or alcohol according to either of the following reactions.

$2\ Al(OR)_{3-y}(OH)y \rightarrow (HO)_y(RO)_{3-y-1}Al\text{-}O\text{-}Al(OR)_{3-y}(OH)_{y-1} + ROH$

or

$2\ Al(OR)_{3-y}(OH)y \rightarrow (HO)_{y-1}(RO)_{3-y}Al\text{-}O\text{-}Al(OR)_{3-y}(OH)_{y-1} + H_2O$

The hydrolysis and condensation reactions continue until substantially all of the alkoxy groups are hydrolyzed, and condensation yields a composition of aluminum-oxygen network containing pendent and terminal hydroxyl groups, having the empirical formula AlO(OH).

In one preferred embodiment of the present invention, the aluminum alkoxide is added to 80°C water in a pressure vessel. After the acid is added, the vessel is sealed, and the mixture is heated under pressure. Using aluminum isopropoxide, heating to 125°C for two hours, the pressure reaches about 50 psi. A clear sol is formed in hours under pressure, compared with days at ambient pressure, and precipitation of insoluble aluminum hydroxide is avoided.

In a preferred embodiment of this invention, an alumina sol condenses to form a gel which is weakly crosslinked, such that when the gel is heated to approximately 60°C in a closed container, it converts back to a clear sol. The reformed sol will gel again within about 72 hours at room temperature. This reversible characteristic provides an alumina sol-gel composition with a relatively long shelf life.

After preparation of the alumina sol, an organoalkoxysilane is added. The organoalkoxysilane reacts with the hydrolyzed alumina sol to form a silicon-oxygen-aluminum network according to the following general reaction.

$AlO(OH) + R_xSi(OR')_{4-x} \rightarrow \text{-}O\text{-}Al\text{-}O\text{-}SiR_x(OR')_{4-x-1} + R'OH$

In an aqueous alumina sol, the remaining alkoxy groups of the organoalkoxysilane are hydrolyzed according to the following general reaction

$\text{-}O\text{-}Al\text{-}O\text{-}SiR_x(OR')_{4-x-1} + (4\text{-}x\text{-}1)H_2O \rightarrow \text{-}O\text{-}Al\text{-}O\text{-}SiR_x(OH)_{4-x-1} + (4\text{-}x\text{-}1)R'OH$

Various organoalkoxysilanes may be used in accordance with the present invention. Organoalkoxysilanes of the general formula $R_xSi(OR')_{4-x}$ wherein x is less than 4 and preferably is one, R is an organic radical, and R' is a low molecular weight alkyl radical are preferred. R is preferably a low molecular weight, preferably from one to six carbon, alkyl or vinyl, methoxyethyl, phenyl, γ-glycidoxypropyl or γ-methacryloxypropyl. R' is preferably a two to four carbon alkyl group. Particularly preferred organoalkoxysilanes are those wherein R is methyl and R' is ethyl; a most preferred organoalkoxysilane is methyl triethoxysilane. The organoalkoxysilane is preferably added in an amount such that the molar ratio of silica (SiO_2) to alumina (Al_2O_3) is from about 10:1 to about 1:1, more preferably from about 6:1 to 3:1. The resulting organosiloxane/alumina sol is useful as a coating composition for application to a substrate surface.

In one embodiment of the present invention, a transparent, colorless organoalkoxysilane/alumina composition may be applied to a plastic transparency by any of a variety of methods such as spinning, spraying, dipping or flowing to form a continuous coating. Upon drying and curing at about 100°C, a durable, glassy coating is formed which improves the surface properties of the plastic transparency. Preferred coating thickness is in the range of about 1 to 20 microns. A coating about 5 microns thick provides a protective surface comparable to a glass surface in abrasion resistance. Bayer abrasion testing of the coated surface involves abrading the coated surface with 1000 grams of quartz sand in the 6 to 14 mesh size range for 300 cycles according to ASTM F-735 and comparing the transmittance and haze before and after abrasion.

In another embodiment of the present invention, pigments may be added to the organoalkoxysilane/alumina sol, which may be applied, dried and cured as a translucent or opaque paint on a variety of substrates. Preferably pigments include inorganic oxides such as colored metal oxides and titania coated mica. Appropriate temperatures for curing the coating depend on the substrate. Preferably, if the coating is applied to acrylic, the temperature is held at about 80°C to 85°C. For coatings on polycarbonate, temperatures of 120°C to 130°C are preferred. Less temperature sensitive substrates, such as glass and metal, can be coated and cured at temperatures in the range of 250°C to 600°C. The higher the temperature, the faster the cure. Preferably, the oragnoalkoxysilane/alumina composition may contain fillers such as talc or mica to adjust the thermal expansion of the coating to match that of the substrate in order to avoid cracking of the coating or crazing of the substrate. A preferred additive is mica in theoretical 3000 mesh particle size of 5 to 10 microns in diameter by 0.5 micron thickness available as Micro Mica C-3000 from The English Mica Co., Stamford, Connecticut.

Preferred organoalkoxysilane/alumina compositions for use as architectural coatings on glass comprise an alumina sol which is between 3 and 16 percent solids, and sufficient organoalkoxysilane to provide a molar ratio of about 10:1 to 1:1, preferably 6:1 to 3:1, silica (SiO_2) to alumina (Al_2O_3). Pigments and fillers may be added up to about a 50 percent solids level. The resulting coating composition is preferably sprayed or flow coated onto a glass sub strate surface. The coated surface may be heated in an oven or under infrared heaters, preferably to at least about 250°F (about 121°C), more preferably to about 500°F (about 260°C), to cure the coating. All of the water and organic solvent is removed, leaving an oxide-containing network, containing pigments and fillers, which is sufficiently dense to survive a durability test consisting of immersion for 24 hours in boiling water. The finish of the coating may be matte if inorganic oxide pigments are used, such as the metal oxide pigments available from the Shepherd Chemical Co. A glossy finish may be obtained by using titania-coated mica pigments, such as the Afflair series from E. & M. Chemical Company. A matte color finish may be made glossy with a clear glassy overcoat of a transparent silane-alumina composition in accordance with the present invention. Preferred opaque coatings on glass range from 7.5 to 12 microns in thickness.

A multi-component organoalkoxysilane/mixed metal alkoxides composition is prepared in accordance with the present invention in order to provide a coating with superior abrasion resistance, as well as alkali resistance and chemical resistance, which can be pigmented and coated on metal, ceramic and glass surfaces, as well as on plastics, and the refractive index of which may be matched to that of a transparent substrate for optical applications.

Preferably, an organoalkoxysilane is first at least partially hydrolyzed by adding a less than equivalent quantity of water to an organoalkoxysilane in solution, preferably in alcohol. The organoalkoxysilane preferably has the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is low molecular weight alkyl radical, and x is at least one and less than 4; preferably x is 1, so that the organoalkoxysilane has three hydrolyzable sites. The organic radical R is preferably a lower (C_1 to C_6) alkyl or vinyl, methoxyethyl, phenyl, γ-glycidoxypropyl or γ-methacryloxypropyl. Preferably, R' is selected from the group consisting of methyl, ethyl, propyl and butyl. Preferred organoalkoxysilanes include those wherein R is methyl and R' is ethyl, particularly methyl triethoxysilane. Another preferred organoalkoxysilane is γ-glycidoxypropyl trimethoxysilane. Mixtures of organoalkoxysilanes may also be preferred. Preferably about one mole of water per mole or organoalkoxysilane is added in alcohol medium to partially hydrolyze the organoalkoxysilane according to the general reaction

$R_xSi(OR')_{4-x} + yH_2O \rightarrow R_xSi(OR')_{4-x-y}(OH)_y + yR'OH$

After the organoalkoxysilane is partially hydrolyzed, additional metal ions are incorporated in the composition by adding hydrolyzable metal alkoxides to the partially hydrolyzed organoalkoxysilane. Preferably, these additional metal alkoxides include alkoxides of the general formula

$M(OR'')_z$

wherein M is a metal selected from the group consisting of aluminum titanium, zirconium and mixtures thereof, z is the valence of M and R" is a low molecular weight alkyl radical, preferably ethyl, propyl or butyl. In addition to aluminum, titanium and/or zirconium, other metal alkoxides including such metals as tantalum, hafnium, etc., may be employed. The metal alkoxide may include an alkyl or aryl group or be in dimer or higher condensed form so long as hydrolyzable alkoxy groups remain reactive with silanol groups of the partially hydrolyzed organoalkoxysilane to copolymerize.

When metal alkoxides or alkylalkoxides are introduced into the partially hydrolyzed organoalkoxysilane, the hydrolyzable alkoxy groups react with the hydroxyl bonds of the partially hydrolyzed organoalkoxysilane, condensing to form an inorganic oxide network and producing alcohol according to the general reaction:

$$-\underset{R}{\overset{OR'}{\underset{|}{\overset{|}{Si}}}} - OH + R''O\text{-}M(OR'')_{z-1} \rightarrow -\underset{R}{\overset{OR'}{\underset{|}{\overset{|}{Si}}}} - O - M(OR'')_{z-1} + R''OH$$

Once the metal alkoxide is reacted with the organoalkoxysilane by this reaction, the composition may be fully hydrolyzed by the addition of water, converting the alkoxy groups OR' and OR" to hydroxyl groups without precipitation of insoluble metal hydroxides. Condensation polymerization proceeds to extend the inorganic oxide network. The composition may then be diluted with either water, alcohol or other suitable solvent to the concentration desired for applying a coating to a substrate. Using titanium alkoxides in

conjunction with zirconi um, aluminum and silicon alkoxides in various ratios provides coatings with refractive indices within the range of 1.4 to 1.85 for optical coating applications.

In a preferred embodiment of the present invention, an alkoxide is partially hydrolyzed before adding an aqueous sol of colloidal cerium oxide. Preferably, the alkoxide is an alkoxysilane of the general formula $R_x Si(OR')_{4-x}$ wherein R is an organic radical, R' is selected from the group consisting of low molecular weight alkyl radicals, and x is less than 4 and may be zero. The organic radical of R is preferably alkyl, vinyl, methoxyethyl, phenyl, γ-glycidoxypropyl, or γ-methacryloxypropyl. The alkoxide hydrolyzes according to the general reactions

$R_xSi(OR')_{4-x}$ + yH_2O $R_xSi(OR')_{4-x-y}(OH)_y$ + $yR'OH$.

Condensation of the hydrolyzed alkoxide proceeds according to the general reaction

$$2R_xSi(OR')_{4-x-y}(OH)_y \longrightarrow \begin{array}{l} R_xSi(OR')_{4-x-y}(OH)_{y-1} \\ \quad | \\ \quad O \\ \quad | \\ R_xSi(OR')_{4-x-y-1}(OH)_y \end{array} + R'OH$$

or

$$2R_xSi(OR')_{4-x-y}(OH)_y \longrightarrow \begin{array}{l} R_xSi(OR')_{4-x-y}(OH)_{y-1} \\ \quad | \\ \quad O \\ \quad | \\ R_xSi(OR')_{4-x-y}(OH)_{y-1} \end{array} + H_2O$$

Further hydrolysis and condensation follow.

The pH and/or degree of condensation of the alkoxides may be adjusted, if necessary, to prevent haze or precipitation upon mixing with the ceria sol. The cerium oxide sol preferably comprises about 10 to 30 percent by weight colloidal cerium oxide in water, with the colloidal cerium oxide particle size sufficiently small to minimize scattering of visible light, preferably less than 30 to 40 nanometers, most preferably less than 10 nanometers. Alkoxides of titanium and/or zirconium may also be included in compositions of the present invention, as well as colloidal silica for abrasion resistance. The ultraviolet radiation protection provided by the cerium oxide containing coating of the present invention may be determined by measuring the UV absorbance spectrum of the coating applied on a quartz substrate.

An aqueous composition of organoalkoxysilane and metal alkoxide is prepared by first partially hydrolyzing an organoalkoxysilane with water. A less than equivalent quantity of water is added to an organoalkoxysilane of the general formula $R_xSi(OR')_{4-x}$wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is at least one and less than four. Preferably x is one, so that the organoalkoxysilane has three hydrolyzable sites. Partial hydrolysis requires, in this case, less than three moles of water per mole of monomeric organoalkoxysilane. Preferably, about one mole of water is added to partially hydrolyze the preferred organoalkoxysilane according to the following general reaction

$R_xSi(OR')_{4-x}$ + $yH_2O \rightarrow R_xSi(OR')_{4-x-y}(OH)_y$ + $yR'OH$

Because the organoalkoxysilane and water are immiscible, a small amount of cosolvent is preferably added. Preferably, a small amount of alcohol is added to promote miscibility and, if necessary, a small amount of catalyst such as nitric acid to accelerate hydrolysis. Preferred organoalkoxysilanes are those wherein x is 1, R is selected from the group consisting of lower (preferably one to six carbon) alkyl or vinyl, methoxyethyl, phenyl, γ-glycidoxypropyl and γ-methacryloxypropyl and R' is selected from the group consisting of methyl, ethyl, propyl and butyl. Mixtures of organoalkoxysilanes may be preferred. It is crucial to the practice of the invention that during the initial partial hydrolysis of the organoalkoxysilane, essentially all of the water is consumed in the hydrolysis step. It is also crucial that the partially hydrolyzed organoalkoxysilane cannot be allowed to stand so long that the condensation polymerization reactions

$$2R_xSi(OR')_{4-x-y}(OH)_y \rightarrow \begin{array}{l} R_xSi(OR')_{4-x-y}(OH)_{y-1} \\ \quad | \\ \quad O \\ \quad | \\ R_xSi(OR')_{4-x-y}(OH)_{y-1} \end{array} + H_2O$$

or

$$2R_xSi(OR')_{4-x-y}(OH)_y \rightarrow \begin{array}{l} R_xSi(OR')_{4-x-y-1}(OH)_y \\ \quad | \\ \quad O \\ \quad | \\ R_xSi(OR')_{4-x-y}(OH)_{y-1} \end{array} + R'OH$$

proceed to eliminate active silanol groups needed for reaction with the titanium or zirconium alkoxides to be added.

The second step involves incorporation of metal ions into the organoalkoxysilane network by the addition of a metal alkoxide of the general formula $M(OR'')_z$ wherein M is preferably titanium or zirconium, R" is a low molecular weight alkyl radical, preferably containing two to four carbons, and z is the valence of M. The metal alkoxide may comprise an alkyl or aryl radical and may be in dimer or higher condensed form so long as the alkoxide contains hydrolyzable groups reactive with silanol groups to copolymerize. Because titanium and zirconium alkoxides also hydrolyze in water, and form insoluble hydroxide species which precipitate from an aqueous medium, the titanium or zirconium alkoxide must be added to the partially hydrolyzed organoalkoxysilane in the essential absence of water. The addition of titanium or zirconium alkoxide to the partially hydrolyzed organoalkoxysilane results in the copolymerization of an inorganic oxide network wherein titanium or zirconium ions are interspersed with silicon according to the following general reaction

$$R_xSi(OR')_{4-x-y}(OH)_y + M(OR'')_4 \rightarrow \begin{array}{l} R_xSi(OR')_{4-x-y}(OH)_{y-1} \\ \quad | \\ \quad O \\ \quad | \\ \quad M(OR'')_{z-1} \end{array} + R''OH \; .$$

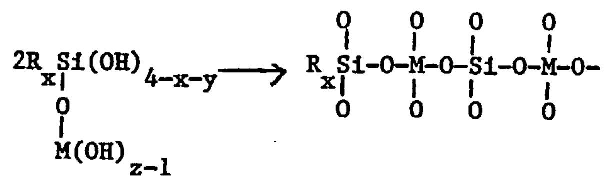
The copolymerization reaction must proceed essentially to completion, i.e., essentially all the titanium or zirconium alkoxide must be reacted into the polymer network. Titanium or zirconium may also be introduced into the partially hydrolyzed organoalkoxysilane in the form of clear polymer solutions wherein hydrolyzable alkoxy groups remain reactive with silanol groups of the partially hydrolyzed organoalkoxysilane.

The final step involves addition of a large quantity of water to essentially completely hydrolyze the composition, i.e., all remaining hydrolyzable groups of either the silane or the titanium or zirconium alkoxide are hydrolyzed according to the general reaction:

$$\begin{array}{l} R_xSi(OR')_{4-x-y} \\ \quad | \\ \quad O \\ \quad | \\ M(OR'')_{z-1} \end{array} + \underset{\text{(in excess)}}{H_2O} \longrightarrow \begin{array}{l} R_xSi(OH)_{4-x-y} \\ \quad | \\ \quad O \\ \quad | \\ M(OH)_{z-1} \end{array} + \underset{\text{(in various quantities)}}{R'OH + R''OH}$$

Because any unincorporated titanium or zirconium alkoxide would hydrolyze to form insoluble hydroxides which would precipitate from the aqueous medium, the water must be added in the essential absence of unreacted titanium or zirconium alkoxide.

The resultant composition is an essentially aqueous organoalkoxysilane/metal oxide sol-gel composition which may be dried and cured to form an inorganic oxide network according to the following condensation polymerization reaction



wherein silicon and metal ions are proportionately dispersed throughout the oxide network. The siloxane/metal oxide polymer may be in the form of a monolithic article, or may be applied as a coating composition to the surface of a substrate to form a glassy film. Applied to a plastic substrate such as polycarbonate or acrylic, a silane/metal oxide coating of the present invention has superior abrasion resistance to that of a silane/alumina or other organic solvent based abrasion resistant coating.

Preferably, the fully hydrolyzed composition is applied by any conventional procedure such as spraying, dipping or flow coating onto a surface of a substrate. The coating composition is dried to remove alcohol and water solvents, and then heated to promote the continued condensation polymerization of the composition, and curing to a dense glassy abrasion resistant film.

However, the inorganic polymer still contains some residual alkoxy groups. When the composition is subsequently fired to densify the inorganic polymer, and residual organic material will be eliminated by thermal decomposition. However, thermal decomposition of residual organic material may result in carbon deposits which blacken the inorganic polymer and degrade the integrity of the metal/oxide network.

In accordance with the present invention, the dried gel, whether in monolithic or coating form, is treated with water or other aqueous solvent, such as inorganic acid or hydrogen peroxide, to remove residual organic material by solid-state hydrolysis before the gel is fired. Thus, the inorganic polymer is not blackened or degraded by carbon deposition. When the composition is dried to remove the solvent, the alcohol and water formed in the hydrolysis and condensation reactions are removed as well.

Substrates which can be improved in their abrasion resistance and other properties with the organoalkoxysilane/metal oxide compositions of the present invention include polycarbonate and acrylic, particularly as used for vehicle transparencies. Abrasion resistance is measured by ASTM F-735 abrasion testing (Bayer abrasion) using 1000 grams of quartz sand of 6 to 15 mesh size range for 300 cycles. Coating compositions of the present invention may also be used on nonplastic susbtrates such as glass, ceramics and metals to improve corrosion resistance or other properties.

Organic-inorganic hybrid polymers in accordance with the present invention are prepared by polymerizing an organic monomer in the presence of an inorganic oxide sol comprising an organoalkoxysilane having an organic functional group capable of reacting with said organic monomer. The functional group of R is selected in accordance with the organic monomer to be subsequently polymerized. A preferred functional group is acryloxy for reaction with an acrylic monomer capable of polymerization to an acrylic polymer. A preferred organoalkoxysilane for producing hybrid polymers is γ-methacryloxypropyl trimethoxysilane.

A coating composition for the pyrolytic deposition of oxide films containing silicon and tin is prepared by hydrolyzing an alkoxysilane in organic solution and adding an organotin compound. The coating composition is preferably sprayed onto a hot glass surface whereupon it thermally reacts to form an oxide film containing silicon and tin.

After the alkoxysilane is at least partially hydrolyzed, an organotin compound is added, preferably one soluble in the solvent of the at least partially hydrolyzed silicon alkoxide composition. Various organotin compounds are suitable provided they contain a moiety capable of condensation reaction with a silanol group. Pre ferred organotin compounds are of the general formula R''_nSnX_{4-n}wherein R'' is an alkyl or aryl radical, preferably a C_3 or C_4 alkyl, X is selected from the group consisting of alkoxy, aryloxy, carboxy, oxy, halo or $-OSnR''_3$, and n is from 1 to 3. Dibutyltin diacetate and dibutyltin dilaurate are preferred. The composition may be further diluted with additional solvents as necessary to accommodate various coating techniques.

In a preferred embodiment of the present invention, glass substrates are heated to a temperature preferably in the range of 250°C to 650°C, more preferably at least about 400°C, and sprayed with an alkoxysilane/organotin sol in accordance with the present invention. The composition thermally reacts on contact with the hot glass surface to form an oxide film containing silicon and tin independently distributed in an oxide matrix. The oxide film of the present invention may be used to mask the iridescence of infrared reflective tin oxide films.

The present invention will be further understood from the descriptions of specific examples which follow.

EXAMPLE 1

An abrasion resistant coating composition is prepared as follows. A solution is prepared comprising 100 grams of γ-glycidoxypropyl trimethoxysilane

$$\overset{O}{(CH_2\text{—}CHCH_2O(CH_2)_3Si(OCH_2)_3)},$$

100 grams of ethyl alcohol, 8 grams of water for hydrolysis and 0.3 grams of nitric acid. The solution is stirred for 10 minutes at room temperature to partially hydrolyze the organoalkoxysilane and completely react the water. A clear sol is formed, to which is added 40 grams of titanium tetraethoxide ($Ti(OC_2H_5)_4$). The mixture is stirred for 20 minutes to completely react the titanium tetraethoxide with the partially hydrolyzed organoalkoxysilane. Finally, an additional 20 grams of water is introduced to complete the hydrolysis of the organoalkoxysilane/titania composition, along with an additional 60 grams of alcohol to adjust the solution concentration to a suitable level for coating application.

A polycarbonate substrate is cleaned, primed with an aminosilane by dipping for 7 minutes into A1120 from Union Carbide, rinsing with 2-propanol then water, and drying for half an hour at 60°C to 80°C. The primed substrate is then immersed into the above-described organoalkoxysilane/titania composition, and withdrawn at a rate of 10 centimeters per minute. The coated substrate is heated to 130°C in an oven and held at that temperature for 2 hours to cure the coating. After cooling to room temperature, the coated substrate is subjected to 300 cycles of Bayer abrasion using 1000 grams of quartz sand of 6 to 14 mesh size. Following the abrasion testing, the coated substrate measures 3.6 percent haze, compared with 60 to 65 percent haze for an uncoated polycarbonate substrate after 300 cycles of Bayer abrasion testing.

EXAMPLE 2

An aqueous sol containing 4.0 percent by weight alumina (Al_2O_3) is prepared by mixing together 174 grams of aluminum isopropoxide ($Al(OC_3H_7)_3$), 900 grams of deionized water and 13 grams of glacial acetic acid. The mixture is stirred for 2 hours at 120°C in a pressure vessel to form a clear sol. To 224.3 grams of the alumina sol are added 22.43 grams of methyl triethoxysilane ($CH_3Si(OC_2H_5)_3$) and 29.74 grams of γ-gycidoxypropyl trimethoxysilane

$$\overset{O}{(CH_2\text{—}CHCH_2O(CH_2)_3Si(OCH_3)_3)}.$$

This mixture is subjected to ultrasonic mixing for half an hour and then mechanical stirring overnight. Finally, 5 grams of deionized water and 2 grams of 2-propanol are added containing 0.9 grams of ammonium perchlorate, NH_4ClO_4, as an epoxy curing catalyst.

A polycarbonate substrate is treated on the surface to be coated with an aminosilane primer available as A1120 from Union Carbide. In this example both surfaces of the substrate are primed for coating by dipping the substrate in the aminosilane primer for 7 minutes, rinsing with 2-propanol and the water, and drying at 60°C to 80°C for about 30 minutes. The primed polycarbonate substrate is dipped into the above-described organosiloxane/alumina composition for 1 minute and air dried for half an hour at ambient temperature. The coated polycarbonate is then placed in an oven for curing of the coating at 60°C for half an hour, followed by 130°C for six hours. After the coated polycarbonate is cooled to room temperature, its optical properties are measured to be 89.3 percent transmittance and 0.5 percent haze. After 300 cycles of Bayer abrasion testing, the coated polycarbonate maintained 87.8 percent transmittance and has 9.7 percent haze, compared with 60 to 65 percent haze for uncoated polycarbonate after 300 cycles of Bayer abrasion testing.

EXAMPLE 3

A partially hydrolyzed organoalkoxysilane sol is prepared by combining 100 grams of γ-glycidoxypropyl trimethoxysilane

$$\begin{array}{l} \quad\;\; O \\ \quad\; / \; \backslash \\ (CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3) \end{array}$$

in 100 grams of ethanol with 8 grams of water and 0.2 grams of nitric acid and stirring for 10 minutes at ambient temperature. To this partially hydrolyzed organoalkoxysilane are added 20 grams of zirconium n-propoxide ($Zr(OC_3H_7)_4^n$) and 10 grams of titanium ethoxide ($Ti(OC_2H_5)_4$). The composition is stirred at ambient temperature for 20 minutes to allow copolymerization of the metal alkoxides with the partially hydrolyzed organoalkoxysilane. Finally, 20 grams of water and an additional 60 grams of ethanol are added to fully hydrolyze the composition and dilute it for coating application.

A polycarbonate substrate is cleaned and primed by dipping in aminosilane (A1120 from Union Carbide) for 7 minutes, rinsing in 2-propanol then water, and drying for 30 minutes at 60°C to 80°C. The primed polycarbonate is then coated by dipping into the coating composition of this example for 1 minute, drying in air at ambient temperature and curing at 130°C for 2 hours. The index of refraction of the coating is 1.6 compared to 1.54 for a comparable coating without the titanium.

EXAMPLE 4

A silane/ceria/silica coating which is both abrasion-resistant and ultraviolet radiation resistant is prepared as follows. An organoalkoxysilane composition is prepared by combining 200 grams of methyl triethoxysilane and 20 grams of dimethyl diethoxysilane. To the organoalkoxysilane are added 120 grams of a colloidal dispersion of silica containing 30 percent by weight of colloidal silica having an average particle size of 13 to 14 nanometers, and 7 grams of glacial acetic acid. This composition is stirred for 3 days to hydrolyze the organoalkoxysilane. The hydrolyzed organoalkoxysilane composition is diluted with 75 grams of iso-butanol. To 50 grams of the diluted hydrolyzed organoalkoxysilane is added 5 grams of an aqueous colloidal dispersion of cerium oxide containing 18 percent by weight colloidal cerium oxide having an average particle size of 5 to 15 nanometers. The sol is adjusted to pH of 5.5 to 6 with 10 drops of triethylamine, and stirred for half and hour at room temperature.

Polycarbonate substrates are primed by dipping for 1 minute in SP-1 acrylic primer from Exxene Chemical Co., drying and curing for 30 minutes at 60°C to 80°C. Primed polycarbonate substrates are then dipped into the above coating composition for 1 minute, air-dried for half an hour, then cured by heating from 40°C to 120°C over a period of one hour and holding at 120°C for 2 hours. A coating is formed having a thickness of about 6.5 microns. After colling to ambient temperature, the coated polycarbonate is exposed to ultraviolet radiation in Q-UV testing for 425 hours. The result is a yellowness index change of 2 compared with a change of 10 for a comparable silane/silica coating without cerium oxide.

EXAMPLE 5

An aqueous organoalkoxysilane/titania composition is prepared as follows. First, to 100 grams of γ-glycidoxypropyl trimethoxysilane are added 40 grams of 2-propanol, 8 grams of deionized water and 10 drops of nitric acid. The mixture is stirred for 15 minutes to complete the partial hydrolysis of organoalkoxysilane without allowing significant condensation polymerization. Next is added 30 grams of tetraethyl titanate. Stirring is continued for 30 minutes to ensure complete reaction of the titanate with the partially hydrolyzed organoalkoxysilane. Finally added are 170 grams of deionized water and 2 grams of ammonium perchlorate to completely hydrolyze the composition. Stirring is continued until a clear sol is formed. Before the composition is applied as a coating, 2 drops of surfactant may be added to promote wetting. A suitable surfactant is Zonyl FSN from DuPont.

A polycarbonate substrate 1/8 inch (about 3 millimeters) thick is primed with an aminosilane by dipping for 7 minutes in A-1120 from Union Carbide, rinsing with 2-propanol then water, and drying for 30 minutes at 60°C to 80°C. The primed substrate is dipped into the above-described composition for 1 minute. After air-drying for half an hour, the coating is heated from 40°C to 130°C over a period of one hour and held at

130°C for 3 hours to cure the coating. After cooling to room temperature, the coated substrate's optical properties are measured as 88.9 percent transmittance and 0.3 percent haze. After Bayer abrasion testing of 300 cycles with 1000 grams of quartz sand of 6 to 14 mesh size according to ASTM F-735, the optical properties of the coated substrate are 88.8 percent transmittance and 2.1 percent haze, compared to 60 to 65 percent haze for uncoated polycarbonate after 300 cycles of Bayer abrasion testing.

EXAMPLE 6

A solution containing 10 percent by weight equivalent of SiO_2 was prepared by dissolving 208 grams of tetraethylorthosilicate (TEOS), $Si(OC_2H_5)_4$, in 320 grams of ethanol, and adding 72 grams (4 moles per mole of TEOS) of water and 0.5 grams of nitric acid. After 24 hours of hydrolysis at 60°C, an aliquot of this sol was dried at 100°C to form a dried gel. The oxide content (SiO_2) of the polysiloxane gel is determined by firing 10 grams of the dried gel at 600°C. In this case, the mass after firing was 8.43 grams for a SiO_2 content of 84.3 percent by weight, and the fired polymer was black as a result of carbon deposition from the residual organic material.

For comparison, a second aliquot of the same sol was dried at 100°C to form a dried gel. Before firing, the dried gel was soaked in water at 100°C for 2 hours. After redrying, 10 grams of the dried gel was fired at 600°C. The resultant mass was 9.7 grams, for a SiO_2 content of 97 percent, and no carbon deposition was observed. Therefore, 1.27 grams of residual organic material was removed by solid-state hydrolysis.

EXAMPLE 7

An organic-inorganic hybrid polymer is prepared as follows. A 5 percent alumina sol is prepared by heating 900 grams of water to 80°C and adding 225 grams of aluminum isopropoxide, $(Al(OC_3H_7)_3)$, and 19.8 grams of glacial acetic acid. Heating at 120°C for 2 hours in a pressure vessel produces a clear alumina sol. To 130 grams of the alumina sol is added an equimolar amount, 15.8 grams, of methacryloxypropyl trimethoxysilane

$$(CH_2 = \overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} -O(CH_2)_3Si(OCH_3)_3).$$

The mixture is stirred, gels in about 45 minutes, and is heated overnight at 60°C. The gel is filtered, rinsed with deionized water and dried overnight at 60°C. One hundred grams of methyl methacrylate plus 0.5 grams of azobisisobutyronitrile catalyst from Dupont are heated in a 70°C water bath for about 14 minutes before adding 11.02 grams of the gel. Ultrasonic stirring for 10 minutes and heating to 70°C for 5 minutes result in a clear solution, which is cooled to ambient temperature and cast in a release-coated glass cell. The compositon is cured by exposure to ultraviolet radiation of 360 nanometers for 90 minutes, followed by heating to 100°C for about 25 minutes. This new polymer has better solvent resistance than poly(methyl methacrylate), does not melt at 260°C and has a Mohs hardness of about 3.

EXAMPLE 8

A partially hydrolyzed alkoxysilane sol is prepared by dissolving 52 grams of tetraethylorthosilicate in 50 grams of 2-propanol, and adding 4.5 grams of water to hydrolyze the alkoxide along with 0.16 grams of nitric acid to promote hydrolysis. The sol is stirred for 30 minutes at 60°C before adding 26.3 grams of dibutyltin diacetate. The alkoxysilane/organotin composition is sprayed on glass sheets at 1180°F (about 638°C) to produce a transparent oxide film containing silicon and tin in a molar ratio of 77/23 and having a luminous reflectance of 14.2 percent.

The above examples are offered to illustrate the present invention. Various organoalkoxysilanes may be employed in accordance with the present invention in a wide range of proportions with various aluminum, titanium, zirconium and other metal alkoxides in different combinations and in a wide range of proportions and concentrations, and cured using different temperatures and cycles to optimize desirable properties in the coating. Additives such as surfactants, wetting agents, ultraviolet radiation absorbers, fillers, pigments and flow control and other additives may be included in coating composi tions of the present invention which may be prepared in a variety of alcohol or other organic solvents, or in essentially aqueous media in any amount which does not interfere with network formation. Various plastic substrates may be coated with

the silane/metal oxide compositions of the present invention e.g. to improve abrasion resistance. Nonplastic substrates such as glass may be painted with pigmented compositions, and metal substrates may be coated with clear or colored compositions, e.g. to improve corrosion resistance or produce spandrel products in accordance with the present invention.

Various hydrolyzable alkoxides and cerium oxide compositions may be combined in a wide range of proportions and concentrations, so long as there is sufficient alkoxide to form an oxide network and sufficient cerium oxide to provide desired improvement in ultraviolet radiation resistance, as measured by the UV absorbance spectrum of the coating on a quartz substrate.

Treatment of a preformed monolith or film of metal oxide formed by metal alkoxide hydrolysis and condensation polymerization is not limited to any particular metal alkoxide sol-gel composition. Various silicon, aluminum, titanium, zirconium and other metal alkoxides and mixtures thereof may be treated with water, inorganic acid, hydrogen peroxide or other suitable aqueous solvent to effect solid-state hydrolysis to an essentially organic-free composition in accordance with the present invention. In some instances where hydrolysis of alkoxides is promoted by a catalyst, it may be desirable to include such a catalyst in the aqueous treatment medium of the present invention. In general, the higher the temperature of the aqueous treatment medium, the faster and more efficient is the removal of residual organic material. In fact, steam may be used to treat gels in accordance with the present invention, and may be particularly useful for treating thin films to produce higher index of refraction, denser materials with greater thermal stability and reduce carbon residue.

Various inorganic compositions containing organic functional groups may be reacted with various organic polymerizable species in a wide range of proportions to obtain a variety of desired properties.

Various hydrolyzable silicon compounds and organotin compounds may be used in a wide range of concentrations and proportions in a variety of solvents, and applied by any suitable coating technique to a variety of substrates which may be heated to sufficient temperature for the thermal reaction of the composition to form an oxide film containing silicon and tin on the substrate surface.

The scope of the present invention is defined by the following claims.

Claims

1. A composition of matter comprising the polymerization reaction product of an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical and x is at least one and less than 4, and an alkoxide of a metal selected from the group consisting of titanium and zirconium.

2. A method of making an organoalkoxysilane-metal oxide composition comprising the steps of:

a. partially hydrolyzing in organic solution an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is at least 1 and less than 4;

b. adding to said partially hydrolyzed organoalkoxysilane an alkoxide of a metal selected from the group consisting of titanium and zirconium;

c. reacting said metal alkoxide with said partially hydrolyzed organoalkoxysilane; and

d. adding additional water to hydrolyze the composition.

3. A composition of matter comprising the polymerization reaction product of the hydrolyzate of an aluminum alkoxide and an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical and x is at least one and less than 4.

4. A method of making an organoalkoxysilane/alumina composition comprising the steps of:

a. hydrolyzing an aluminum alkoxide; and

b. adding to said hydrolyzate an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is at least 1 and less than 4.

5. A composition of matter comprising the polymerization reaction product of an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical and x is at least one and less than 4, and at least two metal alkoxides of the general formula $M(OR'')_z$ wherein M is a metal which forms hydrolyzable alkoxides, z is the valence of M, and R" is a low molecular weight alkyl radical.

6. A method of making an abrasion-resistant coating composition comprising the steps of:

a. partially hydrolyzing an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is low molecular weight alkyl radical, and x is at least 1 and less than 4;

b. adding to said partially hydrolyzed organoalkoxysilane a mixture of metal alkoxides comprising at least two metals;

c. reacting said metal alkoxides with said partially hydrolyzed organoalkoxysilane; and

d. further hydrolyzing and condensing the composition.

7. An optically transparent coating composition for protecting a substrate from ultraviolet radiation comprising:

a. a partially hydrolyzed alkoxide of the general formula $R_xM(OR')_{z-x}$ wherein R is an organic radical, M is selected from the group consisting of silicon, aluminum, titanium, zirconium and mixtures thereof, R' is a low molecular weight alkyl radical, z is the valence of M and x is less than z and may be zero; and

b. colloidal cerium oxide.

8. A method of preparing an optically transparent ultraviolet resistant coating composition comprising the steps of:

a. at least partially hydrolyzing an alkoxide of the general formula $R_xM(OR')_{z-x}$ wherein R is an organic radical, M is selected from the group consisting of silicon, aluminum, titanium, zirconium and mixtures thereof, R' is a low molecular weight alkyl radical, z is the valence of M and x is less than z and may be zero; and

b. adding to said at least partially hydrolyzed alkoxide a colloidal dispersion of cerium oxide.

9. A method of making an organoalkoxysilane/metal oxide sol-gel composition in an aqueous medium comprising the steps of:

a. adding a less than equivalent quantity of water to an organoalkoxysilane of the general formula

$R_xSi(OR')_{4-x}$

wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is at least one and less than 4;

b. partially hydrolyzing said organoalkoxysilane according to the general reaction

$R_xSi(OR')_{4-x} + yH_2O \rightarrow R_xSi(OR')_{4-x-y}(OH)_y + yR'OH$

wherein y is at least one and less than 4-x, until said quantity of water is essentially completely reacted;

c. adding to said essentially anhydrous partially hydrolyzed organoalkoxysilane a metal alkoxide of the general formula $M(OR'')_z$ wherein M is a metal which forms a hydrolyzable alkoxide, R" is a low molecular weight alkyl radical, and z is the valence of M;

d. reacting said metal alkoxide with said partially hydrolyzed organoalkoxysilane according to the following general reaction

$$\begin{array}{l} R_xSi(OR')_{4-x-y}(OH)_y + M(OR'')_z \longrightarrow \\ R_xSi(OR')_{4-x-y}(OH)_{y-1} + R''OH \\ \quad O \\ \quad M(OR'')_{z-1} \end{array}$$

until substantially all of said metal alkoxide has reacted with said partially hydrolyzed organoalkoxysilane to form an oxide network; and

e. adding sufficient water to essentially completely hydrolyze said composition.

10. In a method of forming an inorganic oxide polymer network by a sol-gel process of hydrolyzing an alkoxide to form a sol, condensing the hydrolyzate and drying to form a gel, the improvement which comprises treating the dried gel with an aqueous fluid to remove residual alkoxy radicals by solid-state hydrolysis.

11. An organic-inorganic hybrid polymer comprising the reaction product of

a. an organofunctional alkoxysilane of the general formula $R_xSi(OR'_{4-x}$ wherein R is an organofunctional radical, R' is a hydrolyzable low molecular weight alkyl group, and x is at least one and less than 4; and

b. an organic monomer capable of reaction with the organofunctional moiety of R.

12. A method of making an organic-inorganic hybrid polymer comprising the steps of:

a. hydrolyzing an organofunctional alkoxysilane of the general formula $R_xSi(OR')_{4-x}$ wherein R is an organofunctional radical, R' is a hydrolyzable low molecular weight alkyl group, and x is at least one less than 4;

b. reacting said organofunctional R with a polymerizable organic monomer to form an organic-inorganic hybrid; and

c. polymerizing said organic-inorganic hybrid to form an organic-inorganic hybrid polymer.

13. A coating composition for the pyrolytic deposition of an oxide film comprising silicon and tin which comprises:

a. a partially hydrolized alkoxysilane of the general formula $R_xSi(OR')_{4-x}$ wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is less than 4 and may be 0; and

b. an organotin compound compatible with said partially hydrolyzed silicon alkoxide and capable of thermal reaction to form tin oxide.

14. A method for depositing an oxide film containing silicon and tin on a surface of a substrate comprising the steps of:

a. partially hydrolyzing an alkoxysilane of the general formula $R_x\ Si(OR')_{4-x}$ wherein R is an organic radical, R' is a low molecular weight alkyl radical, and x is less than 4 and may be 0;

b. adding to said partially hydrolyzed alkoxysilane an organotin compound capable of thermally reacting to form tin oxide;

c. applying said partially hydrolyzed alkoxysilane and organotin compound to a surface of a substrate; and

d. thermally reacting said partially hydrolyzed alkoxysilane and organotin compound to form an oxide film containing silicon and tin on said substrate surface.